

Topological Classification of Clusters in Condensed Phases

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A methodology is developed to identify clusters in a bulk phase which are topologically equivalent to certain reference clusters. The selected reference clusters are the Morse clusters with 13 or less atoms and the 13 atom clusters found in an FCC and an HCP crystal phase, consisting of an atom and its 12 nearest neighbours. The first step in using the method requires the bond network of the bulk phase to be identified. The bonds may be identified in terms of the distance between the atom pairs or by using a modified Voronoi decomposition, introduced here. We then search for all the 3, 4 and 5 membered shortest path rings and use these to identify some basic clusters. These basic clusters are then combined to identify the above mentioned Morse and crystal clusters. The larger Morse clusters ($N > 13$) may be identified in terms of the basic clusters and the smaller Morse clusters. This work has important applications in studying the energy landscape of a bulk phase. As an example, results from a limited preliminary study on the hard sphere fluid phase are presented.

I. INTRODUCTION

We consider dense bulk atomic phases. An understanding of the energy landscape of such bulk phases has important applications to vitrification [1], crystallisation [2], protein folding [3] and colloidal dispersions [4]. Due to the large number of degrees of freedom in such systems, a direct approach to these problems is often extremely difficult, even with the use of modern computers. Recently the study of small clusters, of isolated particles, has been the subject of important progress [3, 5]. To date, attempts to bring this progress to bear on bulk phases have been limited. Here we pursue this end. Obviously the identification of clusters, similar to those which in isolation are in an energy minimum, in bulk phases is an important part of the energy landscape problem. Due to their efficient packing [6, 7] and low energy, such clusters should be thermodynamically favoured in supercooled liquids at low temperatures and high pressures [2]. We develop the methodology necessary to identify clusters in a bulk phase, which are topologically similar to given reference clusters. The reference clusters are isolated configurations located at minima in the interparticle potential energy landscape. For the Morse clusters [8, 9] (that we focus on here) the Morse potential is used, which is qualitatively similar to a common Lennard-Jones potential with the additional feature that the range of its potential well may be varied by a free parameter. Many of the reference clusters we focus on are similar to those obtained for configurations of spheres, which minimise the second moment of the mass distribution [7]. We use the notation found in references [8, 9] to denote the various Morse clusters.

The identification of clusters in a bulk phase at finite temperature is not an easy task. The clusters may undergo significant perturbations due to the thermal motions and the stresses induced by the rest of the system. Exactly how large a perturbation may be, before we decide that a cluster is no longer similar to the given reference cluster, is a decision which involves arbitrary choices. The goal is to maximise the permitted perturbation while still excluding configurations that are obviously incorrect. The means by which we pursue this inexact goal will become apparent as the paper proceeds. Regardless of these difficulties, there are many methodologies that could be developed to give excellent results at low enough temperatures or high enough densities. Under such conditions the larger perturbations will be so heavily suppressed that they become insignificant. It is such a methodology that we introduce here.

II. SHORTEST PATH RINGS

Our method makes use of 3, 4 and 5 membered shortest path (SP) rings [10]. A shortest path ring is defined in terms of the shortest distance, D , between a pair of atoms. If two atoms are bonded together this distance is $D = 1$ and if two atoms are not bonded but they are both bonded to a common third atom then $D = 2$, etc. An n membered ring has n atoms which are bonded together to form a ring. To understand what a shortest path ring is we consider n atoms, taken from a bulk phase, which form an n membered ring. In isolation the n membered ring forms a n

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membered graph. The bulk phase, consisting of N atoms, also forms a graph. If the distance between each of the atoms in the graph n is the same as the distance between the same atoms in the graph N and each atom in graph n has exactly two bonds the ring is a shortest path ring. We denote an n membered shortest path ring as SPn .

III. DETERMINING THE BOND NETWORK

The simplest way to determine the bond network (what was referred to as a graph in section II) is to label any pair of atoms which are closer together than some distance r_b as bonded. This method can be useful when the pair potential between the two particles features an attractive well which is deeper than several $k_B T$ such as in a colloidal gel phase. Such an approach is not so useful for a dense supercritical fluid phase which is commonly used as a model to study vitrification and crystallisation.

To handle this type of system it is necessary to use a different method to determine the bond network. The standard Voronoi decomposition [11, 12] is not suitable for the identification of $SP4$ rings. For this reason we need to modify the Voronoi method. First let us consider a method by which a bond network may be established from a Voronoi tessellation. The network consists of N atoms where each atom is labelled by the index i . In the Voronoi tessellation each atom is assigned the volume in its immediate neighbourhood consisting of the space which is closer to it than to any of the other atoms. The surface of this volume is composed of flat polygons shared between two atoms. If two atoms share a surface and the line which connects their centres intersects this surface we define them as bonded, otherwise they are not. Let us assume that all the bonded atoms are separated by some length less than r_c which may be made as large as necessary. We start with the atom $i = 1$ and iterate up. We construct the set of atoms, S_i , by finding all the atoms that are within distance r_c of atom i . The position of a given atom is represented by \mathbf{r}_i and the atoms in S_i are ordered starting with the atom closest to i . We iterate through the atoms in S_i using the index k (from closest to furthest from i), and construct the vector $\mathbf{u} = \mathbf{r}_k - \mathbf{r}_i$. We eliminate from S_i all the atoms, that are further from i than k is, and that are on the other side of the plane (relative to \mathbf{r}_i) that is perpendicular to \mathbf{u} and contains the point \mathbf{r}_k . We then continue eliminating atoms from S_i by iterating up through k . The atoms which remain in S_i are bonded to i and, of course i is bonded to the atoms which remain in S_i . We can then iterate i and continue until all the bonds have been established. In mathematical form, atoms i and j are not bonded if they do not satisfy the inequality,

$$\mathbf{r}_i \cdot \mathbf{r}_k + \mathbf{r}_j \cdot \mathbf{r}_k < \mathbf{r}_k \cdot \mathbf{r}_k + \mathbf{r}_i \cdot \mathbf{r}_j, \quad (1)$$

for any of the other atoms k .

The problem with using the standard Voronoi method to identify $SP4$ rings can be appreciated by considering a ring formed by placing atoms exactly on the corners of a perfect square. For such an arrangement to form an $SP4$ ring the atoms on opposite corners must not be bonded. Using Eq. 1 we see that if atoms i and j are on opposite corners, with atom k being one of the remaining two atoms, we have $\mathbf{r}_i \cdot \mathbf{r}_k + \mathbf{r}_j \cdot \mathbf{r}_k = \mathbf{r}_k \cdot \mathbf{r}_k + \mathbf{r}_i \cdot \mathbf{r}_j$ and thus there will be many instances where we fail to identify $SP4$ rings which are required.

To overcome this we modify the previous algorithm. As a first step we consider what happens if we eliminate atoms that are past the plane which is perpendicular to \mathbf{u} and contains the point $f_c \mathbf{r}_k$, where f_c is some arbitrary parameter. This allows us to move the plane closer to the i th atom and eliminate bonds which are impeding the identification of the required $SP4$ rings. Thus we eliminate atoms which fail to satisfy the following inequality,

$$\mathbf{r}_i \cdot \mathbf{r}_i - \mathbf{r}_i \cdot \mathbf{r}_j - \mathbf{r}_i \cdot \mathbf{r}_k + \mathbf{r}_j \cdot \mathbf{r}_k < f_c (\mathbf{r}_i \cdot \mathbf{r}_i + \mathbf{r}_k \cdot \mathbf{r}_k - 2\mathbf{r}_i \cdot \mathbf{r}_k). \quad (2)$$

It is easy to see that Eq. 2 reduces to Eq. 1 when $f_c = 1$. As it stands this procedure has a serious flaw. If we swap the indices i & j , in Eq. 2, when $f_c \neq 1$ we may get a different answer: i.e. atom i may be bonded to atom j while atom j is not bonded to atom i . The inequality, after we swap the indices, is

$$\mathbf{r}_j \cdot \mathbf{r}_j - \mathbf{r}_i \cdot \mathbf{r}_j + \mathbf{r}_i \cdot \mathbf{r}_k - \mathbf{r}_j \cdot \mathbf{r}_k < f_c (\mathbf{r}_j \cdot \mathbf{r}_j + \mathbf{r}_k \cdot \mathbf{r}_k - 2\mathbf{r}_j \cdot \mathbf{r}_k). \quad (3)$$

We can add these two inequalities together to obtain,

$$\mathbf{r}_i \cdot \mathbf{r}_i + \mathbf{r}_j \cdot \mathbf{r}_j - 2\mathbf{r}_i \cdot \mathbf{r}_j < f_c (\mathbf{r}_i \cdot \mathbf{r}_i + \mathbf{r}_j \cdot \mathbf{r}_j + 2\mathbf{r}_k \cdot \mathbf{r}_k - 2\mathbf{r}_i \cdot \mathbf{r}_k - 2\mathbf{r}_j \cdot \mathbf{r}_k), \quad (4)$$

which remains symmetric upon exchanging indices i and j . We may use this criteria Eq. 4 in place of criteria Eq. 1 and tune the value of f_c so that we identify the $SP4$ rings appropriately. Here we set the arbitrary parameter f_c to some value less than unity $f_c < 1$ in an attempt to optimise the effective identification of the clusters which is our goal. If we set $f_c = 1$ we regain the standard Voronoi method.

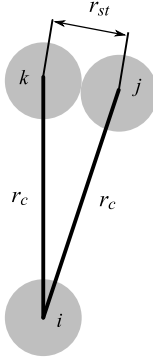


Figure 1: Atoms k and j are as close together as their steric interaction will permit, r_{st} , and are both the same distance from atom i , namely r_c .

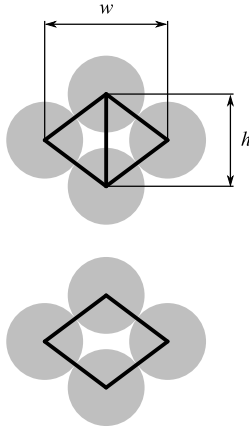


Figure 2: Atoms arranged on the corners of a rhombus with height h and width w . The atoms could be identified as forming two SP3 rings as shown above or as forming a single SP4 ring as shown below. Which of these possibilities is identified will depend on the choice of f_c appearing in Eq. 4.

It is necessary to be careful not to make f_c too small. Consider the three atom system shown in Fig 1 where we might expect that atoms j and k are bonded to atom i . However if f_c is lower than the following value,

$$f_c = \frac{1}{1 + 2 \sin^2(\theta)}$$

$$\theta = 2 \sin^{-1} \left(\frac{r_{st}}{2r_c} \right), \quad (5)$$

given in terms of the distance, r_c , of atom j or k from atom i , and the distance, r_{st} , between the two atoms j & k , (in Fig. 1 depicted as the closest distance the steric interaction will allow) then atoms j & k will not be identified as bonded to i . As our algorithm assumes atoms can only be eliminated from S by considering atoms k which are closer to atom i than j we must choose a value for r_c which is less than that obtained from Eq. 5.

To demonstrate how our modified Voronoi criteria can effectively identify SP4 rings we consider four atoms which are all located in the same plane, forming a rhombus, Fig 2. The rhombus is characterised by the ratio h/w . Using the standard Voronoi method, $f_c = 1$, the only rhombus that will be identified as forming an SP4 ring is a square $h/w = 1$. As we reduce the value of f_c from unity, more asymmetric rhombuses are identified as forming an SP4 ring. If $f_c = 0.9$ the most asymmetric rhombus which will be identified as forming an SP4 ring is $h/w = 0.9045$ and the

maximum radius for bonding to atom i as depicted in Fig. 1 with the minimum separation distance set to $r_{st} = 0.9$ is $r_c \simeq 3.791$. For $f_c = 0.8$ we have $h/w = 0.8165$ and $r_c \simeq 2.504$. The minimum value of h/w for which the disks depicted in Fig. 2 will not overlap is $h/w = 0.5774$ which would require a value of $f_c = 0.5$ to be identified as forming an SP4 ring.

IV. IDENTIFYING THE CLUSTERS

To identify the clusters we will assume that many of the possible configurations can be discounted due to the steric interaction between the atoms. The effective use of this assumption, in terms of what may be discounted, has been refined by trial and error, both in terms of identifying the various clusters in isolation and by applying the code to actual data and checking the results using molecular viewing software. The strategies used to identify the clusters can depend on the method used to establish the bond network. We have successfully employed two methods. First declaring atoms to be bonded when they are very close to the minimum separation distance allowed by their steric interaction. We have used this method to good effect in analysing microscopy data obtained from colloidal gels [4]. These gels feature a potential interaction between the colloidal particles which have a very narrow deep well, providing a natural bond length. Secondly we have used the modified Voronoi method with the parameter $f_c = 0.82$ (see Eq. 4) and the cutoff radius $r_c = 2.0$ for the results reported in section VI here.

After identifying a cluster we store the indices of its atoms which are used later in the final analysis. For this reason any redundant identification of clusters will not concern us. The description below makes no effort to describe how things may be computed efficiently. Rather it attempts to be concise.

Below we describe the features of the various clusters which are used to identify them. The reader may find it helpful to obtain the configuration files for the various clusters [9], and refer to the way they are formed from the various basic clusters using a molecular viewing program. A few example images are provided in Fig 4.

The Basic Clusters

After obtaining the bond network we identify all the SP3, SP4 and SP5 rings in the system. A method by which this may be done is given in reference [10]. We then divide each of the rings, of a given size, into a further three types. For the first of these there are an additional two atoms which are bonded to each atom in the ring. We assume that the steric interaction is such, that the only way this can occur is for one atom to be bonded on each side of the ring (see Fig. 3), and that it is not possible to have more than two atoms bonded to all the atoms forming one of these rings. We will denote such clusters as SP nc where n is the number of atoms in the SP ring. These SP nc clusters correspond to the first three Morse clusters, which we have now succeeded in identifying. Using the notation given in [8, 9] we have SP3c = 5A, SP4c = 6A and SP5c = 7A. The next type of basic cluster we identify is a ring that has only one additional atom bonded to all its atoms. We denote such a cluster as SP nb . Note that the 4 atoms forming an SP3b cluster form a total of 4 SP3b clusters. This redundancy will not concern us. All rings which have no additional atoms bonded to all of their atoms are labelled as an SP na cluster.

The additional two atoms forming an SP nc cluster will be referred to as the spindle atoms. Under the definitions given here, it is possible that these two spindle atoms are or are not bonded to each other. The single additional atom of the SP nb clusters is also referred to as a spindle atom.

One could take an SP nc cluster and find it contains SP nb and SP na clusters. By construction we have imposed the restriction that a given SP n ring is used to form one cluster only, be it type a, b or c. For the larger clusters, that we deal with next, no restriction will be made about whether they are contained in other clusters or not.

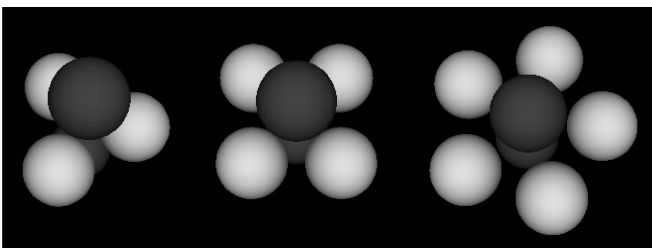


Figure 3: The SP nc clusters. The spindle atoms are dark and the ring atoms are light. From left to right we have SP3c/5A, SP4c/6A, SP5c/7A.

The Eight and Nine Membered Clusters

The first of the eight membered clusters is the 8A Morse cluster, see Fig. 4. We chose to identify this in terms of SP5 rings. It is also possible to identify it in terms of SP4 rings which could be a good choice when using the modified Voronoi method, depending on the value chosen for f_c . If desired, one could do both. The method we use here will sometimes identify the same structure twice, but we are not concerned with this as we can correct for it later. We first search through all possible pairs of SP5b clusters. If we find a pair which has different spindle atoms, s_1 & s_2 , and 4 atoms which are common to both the SP5 rings we label the 8 atoms as forming an 8A cluster. We then search all pairs of SP5c clusters and any pair which has in common the two spindle atoms and 4 SP5 ring atoms, with the 5th ring atoms distinct (i.e. a member of only one of the pair of basic clusters under consideration), is labelled as forming an 8A cluster. Finally we search all pairs composed of one SP5b and one SP5c cluster. If the SP5b spindle atom is also a spindle atom for the SP5c cluster and there are 4 common SP5 ring atoms we label it an 8A cluster.

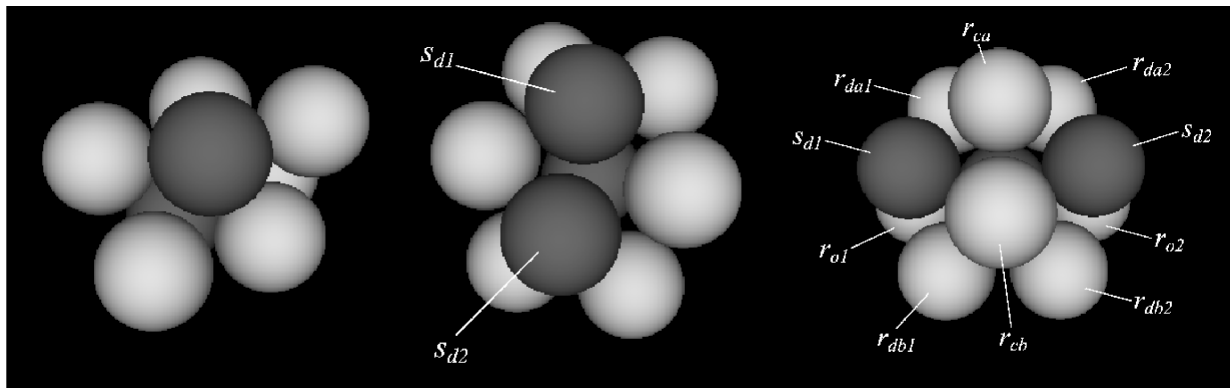


Figure 4: On the left is the 8A cluster with the spindle atoms of the SP5c or SP5b clusters coloured dark. In the middle is the 9B cluster with the two distinct spindle atoms labelled and the common spindle atom s_{com} (coloured dark) partially visible around the back. On the right is the 11C/11D cluster with all of the atoms labelled except for the common spindle atom s_{com} which is the dark one partially visible, centre back.

The 8B cluster is composed of an SP5c cluster and one additional atom. For every SP5c cluster we search through all the other atoms and each time we find one which is bonded to two of the SP5 ring atoms and one spindle atom we have found an 8B cluster.

The 9A cluster is formed from a triplet of SP4b clusters. All combinations of three SP4b clusters are searched to find those which have shared atoms and bonds between the atoms from the three SP4 rings consistent with the 9A cluster. In addition it is checked that the spindle atoms are distinct and not bonded to each other.

The 9B cluster is formed from a pair of SP5c clusters, Fig. 4. The pair has one spindle atom which is common to both basic clusters, s_{com} , and the other two spindle atoms are distinct and bonded to each other (s_{d1}, s_{d2}). The two distinct spindle atoms are members of the other basic cluster's SP5 ring. The two SP5 rings have two atoms in common. Each pair of SP5c rings are checked for these conditions.

The Ten and Eleven Membered Clusters

The 10A cluster is formed from a pair of SP4b clusters. None of the atoms are common and the spindle atoms are not bonded to any of the other basic cluster's atoms. Each atom of one SP4 ring is bonded to two atoms of the other SP4 ring.

The 10B cluster is composed of three SP5c clusters. It is also composed of three 9B clusters. We start with an 9B cluster and search all SP5c clusters which have an index higher than both the SP5c clusters forming the 9B cluster. This ensures we don't search the same combinations more than once. One of the new SP5c cluster's spindle atoms is common to the common spindle atom in the 9B cluster, s_{com} . The other spindle atom, s_{d3} , is bonded to both the distinct spindle atoms of the 9B cluster forming the SP3 ring (s_{d1}, s_{d2}, s_{d3}).

The 11A cluster contains SP4 rings with bond lengths which are not particularly close together. For this reason it is not well suited to identification by the bond length method, although it can work, the Voronoi method will be superior for this case. Pairs of SP4c clusters are searched. The clusters have a common spindle atom, s_{com} , with all other atoms being distinct. Each of the SP4 ring atoms is bonded to 2 atoms from the other SP4 ring.

The 11B cluster is formed from an 9B cluster and two additional atoms, (e_1, e_2) . These two additional atoms are bonded to the common spindle atom of the 9B cluster, s_{com} , and bonded to each other. The two extra atoms also form four bonds with four different atoms from the two SP5 rings. These four SP5 atoms form two pairs which are bonded to each other with no bonds across the pairs.

The 11C and 11D clusters are equivalent for our purposes. They can be formed from two SP5c clusters with one common spindle atom s_{com} . The other two distinct spindle atoms are not bonded, s_{d1} & s_{d2} . The two SP5 rings have two common atoms which are bonded to each other (r_{ca}, r_{cb}) . There are two bonds, between the distinct atoms from the two different SP5 rings, involving four atoms, (r_{da1}, r_{da2}) & (r_{db1}, r_{db2}) . See Fig. 4.

The 11E cluster looks somewhat different to the clusters we have considered so far. None the less it can be constructed by combining an 9B cluster with an additional SP5c cluster. One of the spindle atoms of the SP5c cluster, s_{com2} , is common with one of the distinct spindle atoms from the 9B cluster, $s_{com2} = s_{d1}$. The other spindle atom, s_{d3} , of the new SP5c cluster is bonded to the other distinct spindle atom, s_{d2} , and also bonded to the common spindle atom, s_{com} , of the 9B cluster.

The 11F cluster can be formed from a combination of two SP3c and two SP4c clusters. To identify it we first search through all pairs of SP3c clusters. The spindle atoms of the SP3c clusters are distinct and are all bonded to one of the spindle atoms from the other cluster. Thus we have two bonded pairs of spindle atoms (s_{t1}, s_{t2}) & (s_{b1}, s_{b2}) . The SP3 rings have one common atom, r_{com} , and one bonded pair of distinct atoms from the different SP3 rings (r_{c1}, r_{c2}) . The SP4c clusters have r_{com} as one of their spindle atoms with the other spindle atom being new, s_{e1} and s_{e2} . The SP4 ring of the first SP4c cluster consists of $(r_{c1}, r_{c2}, s_{t1}, s_{t2})$ and that of the second cluster consists of $(r_{c1}, r_{c2}, s_{b1}, s_{b2})$.

The Twelve and Thirteen Membered Morse Clusters

The 12A cluster may be formed from an 11C cluster with one additional atom. The two rings, from the SP5c clusters we used to form the 11C cluster, each have one atom that is not bonded to either of the rings common atoms (r_{ca}, r_{cb}) : we label this pair of atoms, r_{o1}, r_{o2} , see Fig 4. The extra atom is only bonded to three atoms from the 12A cluster which are s_{com}, r_{o1}, r_{o2} .

The 12B and 12C clusters are the same for our purpose. They are essentially an icosahedral cluster with one atom missing. This can be formed from six SP5c clusters. There will be one central SP5c cluster with one common spindle atom s_{com} and one distinct s_{dis} . If we can find an additional five SP5c clusters which have one spindle atom given by s_{com} and the other spindle atom bonded to s_{dis} we have a 12B/12C cluster.

The 12D cluster is formed from an 11E cluster combined with an additional SP5c cluster. The new SP5c cluster has one spindle atom which is common with s_{d3} and the other is common with s_{d2} of the 11E cluster.

The 12E cluster is formed from an 11F cluster combined with an SP3c cluster. The SP3c cluster has the s_{e1} and s_{e2} atoms, of the 11F cluster, as its spindle atoms

The 13A cluster is an icosahedral cluster. It can be formed from an 12B/12C cluster combined with an additional SP5c cluster. One of the additional SP5c's spindle atoms is s_{com} . The other spindle atom and all of the SP5 ring atoms are distinct from the central SP5c cluster of the 12B/C cluster.

The 13B cluster is formed from two SP5c clusters. There is one common spindle atom, s_{com} , with the other spindle atoms being distinct and not bonded to each other. Every atom from the SP5 ring of the first cluster is bonded to exactly one atom from the SP5 ring of the second cluster.

The FCC and HCP Crystal Clusters

The HCP cluster is formed from three SP3c clusters. The three SP3 rings have one atom in common, r_{com} , which is the only atom any of the SP3c clusters have in common. The spindle atoms form two SP3 rings, (s_{a1}, s_{a2}, s_{a3}) & (s_{b1}, s_{b2}, s_{b3}) . Apart from the common atom, r_{com} , the spindle atoms are not bonded to any of the rings atoms from the other SP3c clusters. Upon excluding, r_{com} , from the SP3 rings of the three SP3c clusters we are left with six atoms which form a six membered ring. This ring is not a shortest path ring.

The FCC cluster can be formed from four SP3b clusters or from three SP3b clusters and one SP3c cluster. The first three SP3b clusters all have a common SP3 ring atom, r_{com} , and the spindle atoms are all distinct forming an SP3 ring, (s_{a1}, s_{a2}, s_{a3}) . Excluding r_{com} we are left with six atoms from the SP3b clusters SP3 rings, which form a six membered ring. Again the six membered ring is not a shortest path ring and when we combine it with atom r_{com} we obtain six SP3 rings. Three of these rings are from the initial SP3b clusters and three are not. We will refer to the later as the three new SP3 rings. The fourth SP3b cluster or the SP3c cluster has r_{com} as a spindle atom. Each of its SP3 ring atoms can be combined with a different new SP3 rings to form an SP3b cluster. If an SP3c cluster is used the second spindle atom is not part of the FCC cluster.

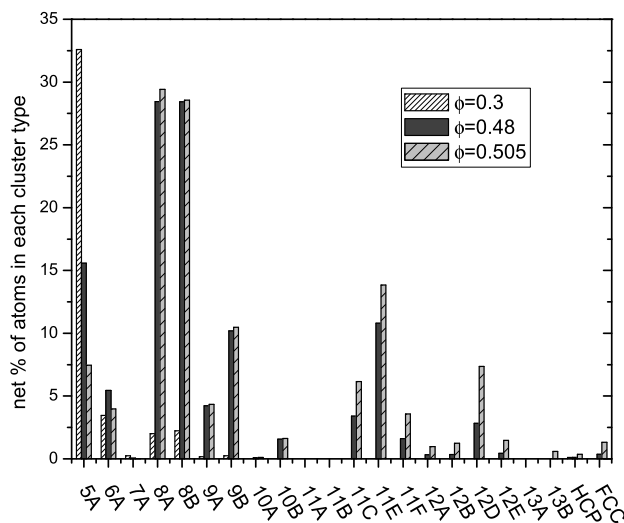
V. ANALYSING THE RESULTS

It is a simple matter to record the atoms which form the various clusters. If some of the clusters have been identified multiple times this can be checked for and corrected later.

However the reporting of population levels for the various clusters opens up choice and ambiguity. This is because a given atom may be a member of several different clusters. We have decided to report the population levels in the following manner. If an atom is a member of a cluster and also a member of a different cluster which has more atoms it is only identified with the larger cluster. An atom may be a member of two clusters consisting of the same number of atoms, in this case the atom is reported as being a member of both clusters if it is not a member of any larger clusters. Using this approach we can construct a histogram of the net population levels for the various clusters.

VI. AN ILLUSTRATION: THE HARD SPHERE FLUID

Hard spheres are seen as a basic reference model for the liquid state whose structure is determined by the short range repulsive interaction between the constituent atoms. This idea can be traced back to van der Waals and was later developed, in the form of perturbation theory, to the point where it could quantitatively account for the properties of real simple liquids [13]. At high densities (volume fractions) the efficient packing of the crystal phase results in more



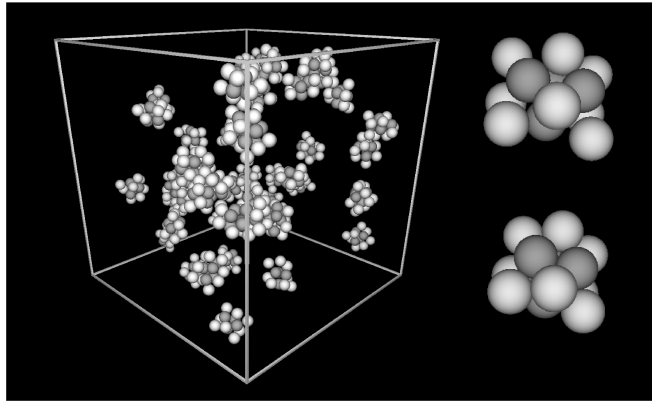


Figure 6: On the left: the atoms which have been identified as members of a 12D cluster from the $\phi = 0.505$ configuration. Four SP5c clusters can be found in a 12D cluster, the spindle atoms from these SP5c clusters are the darker coloured atoms. If an atom is a spindle cluster in one 12D cluster and not in another it is still labelled with the dark colour. Top right is a close up of one of the clusters from the configuration and the bottom right is the configuration of the 12D Morse cluster obtained from [9].

Because the 12D clusters from the $\phi = 0.505$ configuration are the largest clusters identified in significant numbers and because they are somewhat different to the icosahedral clusters that might be expected [18] we focus on these. In Fig. 6 an image of the atoms which have been identified as members of 12D clusters is shown. A close up of one of these clusters is also shown. This cluster was chosen from the configuration at random. For comparison an image of the actual Morse cluster configuration, taken from ref. [9], is also shown. The similarity, in the way the atoms are arranged in both cases, can be readily recognised from these images. Experience of inspecting the various clusters suggests that this is regularly the case.

VII. CONCLUSIONS

A new methodology to identify local structure in dense phases has been introduced. This shows how studies on small isolated clusters of atoms can provide important new insight into our understanding of bulk phases. Because a given atom can be a member of several different clusters the clusters may overlap and fill space. Remarkably some 99% of the atoms in a hard sphere fluid, marginally above the freezing volume fraction, are identified as being a member of at least one of the Morse clusters. As the volume fraction is increased, still more atoms will be identified as cluster members. This demonstrates the promise of the approach, introduced here, as a powerful new tool to further our understanding of bulk phases. In particular one would expect important findings about supercooled liquids, vitrification and possibly crystallisation to be made in the future using this methodology.

Acknowledgments

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- [1] P. G. Debenedetti and F. H. Stillinger, *Nature* **410**, 259 (2001).
 - [2] D. Frenkel, *Nat. Mater.* **5**, 85 (2006).
 - [3] D. J. Wales, *Energy Landscapes: Applications to Clusters, Biomolecules and Glasses* (Cambridge University Press, Cambridge, 2004).
 - [4] C. P. Royall, S. R. Williams, T. Ohtsuka, and H. Tanaka, to be submitted (2007).
 - [5] J. A. Alonso, *Structure and Properties of Atomic Nanoclusters* (World Scientific, Singapore, 2005).
 - [6] N. J. A. Sloane, R. H. Hardin, T. D. S. Duff, and J. H. Conway, *Discrete Comput. Geom.* **14**, 237 (1995).
 - [7] V. N. Manoharan, M. T. Elsesser, and D. J. Pine, *Science* **301**, 483 (2003).
 - [8] J. P. K. Doye, D. J. Wales, and R. S. Berry, *J. Chem. Phys.* **103**, 4234 (1995).

- [9] Coordinate files for the morse clusters may be found at <http://physchem.ox.ac.uk/~doye/jon/structures/Morse/tables.html>.
- [10] D. S. Franzblau, Phys. Rev. B **44**, 4925 (1991).
- [11] J. D. Bernal and J. L. Finney, Discuss. Faraday Soc. **43**, 62 (1967).
- [12] J. L. Finney, Proc. R. Soc. London, Ser. A **319**, 479 (1970).
- [13] J. A. Barker and D. Henderson, Rev. Mod. Phys. **48**, 587 (1976).
- [14] W. G. Hoover and F. H. Ree, J. Chem. Phys. **49**, 3609 (1968).
- [15] P. G. Bolhuis, D. Frenkel, S. C. Mau, and D. A. Huse, Nature **388**, 235 (1997).
- [16] S. R. Williams, G. Bryant, I. K. Snook, and W. van Megen, Phys. Rev. Lett. **96**, 087801 (2006).
- [17] F. Höfling and T. Franosch, Phys. Rev. Lett. **98**, 140601 (2007).
- [18] F. C. Frank, Proc. R. Soc. Lond. A. **215**, 43 (1952).